

A. S. Urusova, A. V. Bryuzgina,
T. V. Aksenova, V. A. Cherepanov

*Institute of Natural Sciences,
Kuybisheva 48 St., Ekaterinburg*

Phone: +79527271271;

E-mail: anastasiyapodzorova@yandex.ru

Crystal structure and oxygen nonstoichiometry of oxides in the Ba-Me-Me'-Y-O (Me, Me'=Co, Fe) system

Polycrystalline $\text{BaMe}_{1-x}\text{Y}_x\text{O}_{3-\delta}$ (Me=Co, Fe) samples were synthesized by a conventional route and glycerol-nitrate technique. According XRD patterns of single phase solid solutions $\text{BaCo}_{1-x}\text{Y}_x\text{O}_{3-\delta}$ ($0.1 \leq x \leq 0.4$) and $\text{BaFe}_{0.9-y}\text{Y}_{0.1}\text{Co}_y\text{O}_{3-\delta}$ ($0.05 \leq y \leq 0.15$) were indexed using $Pm\bar{3}m$ space group. The unit cell parameters were refined using Rietveld full-profile analysis. Oxygen non-stoichiometry of these solid solutions was measured by means of thermogravimetric technique within the temperature range 298–1273 K in air.

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Introduction

Compounds with a perovskite structure currently provoke great interest, due to the unique physical and chemical properties. The prospect of using these compounds as electrode materials of high-temperature fuel cells and catalysts for

exhaust gas after burning, pose aims for optimizing the conditions of their synthesis and complex study of their properties. The objects of this study are doped by B-sublattice cobaltites $\text{BaCo}_{1-x}\text{Y}_x\text{O}_{3-\delta}$ and barium ferrite $\text{BaFe}_{1-x}(\text{Co}, \text{Y})_x\text{O}_{3-\delta}$.

The experimental part

Synthesis of samples for research in system Ba-Me-Me'-Y-O (Me, Me' = Co, Fe) was carried out by standard ceramic technology, and mortar method with the use of glycerine as the organic precursor. Under the standard ceramic technology, the mixture of raw materials with defined components ratio was thoroughly grinded and subjected to a graduated

thermal treatment. The final annealing was carried out for 120 hours at 1373 K in air with intermediate chafing. In the synthesis with precursors, linkages of the initial components were dissolved in nitric acid while heated. Next, an equimolar amount of glycerine was added to the solution, and it was evaporated. The dry residue was slowly heated over the

temperature range 873–1373 K. Further annealing was carried out at a temperature of 1373 K during 60 hours, followed by its cooling the samples to room temperature with the speed 100° per hour. For determining the phase composition, the samples were analyzed by X-ray powder diffraction, using DRON-6 and InelE-quinnox 3000 in $\text{Cu}_{K\alpha}$ -radiation ($\lambda = 1.5418 \text{ \AA}$). Filming was carried out in a range of angles $10^\circ \leq 2\Theta \leq 100^\circ$ at speed from 1.0 to 0.02 degree per minute with a shutter at a point from 1 to 10 seconds. Identification of the phases was carried out using filing JSPDS and software "fpeak". The

unit cell parameters of single-phase oxides were calculated in the program "Cel-ref 3" and refined by full-profile Rietveld analysis in the program "Fullprof 2008". Oxygen non-stoichiometry of complex oxides in the system Ba-Me-Me'-Y-O (Me, Me' = Co, Fe) was studied by high-temperature thermogravimetry as a function of the temperature in the range of $298 \leq T, \text{ K} \leq 1373$, at a pressure of $P_{\text{O}_2} = 0.21 \text{ atm}$, on the machine STA 409 PC. The absolute values of the oxygen non-stoichiometry were determined by direct recovery of samples in hydrogen flow and iodometric titration.

Results and Discussion

Barium cobaltite and ferrite, $\text{BaCoO}_{3-\delta}$, $\text{BaFeO}_{3-\delta}$, respectively, were synthesized by solid-phase synthesis. According to XRD, it was revealed that the complex oxides slowly cooled from 1373 K to room temperature in air are single phased. X-ray data for $\text{BaCoO}_{3-\delta}$ were well described in the hexagonal cell (pr. c. $P6_3 / \text{mmc}$), with parameters: $a = b = 5.665 \text{ \AA}$, $c = 28.493 \text{ \AA}$. Whereas barium ferrite $\text{BaFeO}_{3-\delta}$ radiographic data were described in the orthorhombic cell (pr. c. $P21212$), with parameters: $a = 5.958 \text{ \AA}$, $b = 16.502 \text{ \AA}$, $c = 11.008 \text{ \AA}$. It has been found that administration of yttrium into cobalt or iron sublattice leads to the formation of solid solutions $\text{BaMe}_{1-x}\text{Y}_x\text{O}_{3-\delta}$ (Me = Co, Fe), stabilizing a cubic perovskite structure. For determining the homogeneity of oxides $\text{BaMe}_{1-x}\text{Y}_x\text{O}_{3-\delta}$ (Me = Co, Fe) by solid-phase synthesis, the samples in the composition range $0.0 \leq x \leq 0.6$ in steps of 0.05 were prepared. According to the results of XRD, it was found that the one-phase complex oxides

$\text{BaCo}_{1-x}\text{Y}_x\text{O}_{3-\delta}$ are formed in the range of $0.1 \leq x \leq 0.4$ (Fig. 1.); the replacement of ferrum into yttrium, there is formed only one single-phase oxide $\text{BaFe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$.

Diffraction patterns of single-phase samples were indexed within the cubic cell, space group $Pm\bar{3}m$. As an example, Fig. 2 shows the X-ray $\text{BaCo}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$, treated by the method of full-profile Rietveld analysis.

Increase of yttrium content replacing cobalt in complex oxides $\text{BaCo}_{1-x}\text{Y}_x\text{O}_{3-\delta}$ leads to an increase of the parameter a and the unit cell volume, which can be attributed to the size effects: $r_{\text{Y}}^{3+} = 0.9 \text{ \AA}$ (cn = 6) and $r_{\text{Co}}^{3+} / r_{\text{Co}}^{4+} = 0.61 / 0.53 \text{ \AA}$ (cn = 6)².

To determine the feasibility of the substitution of iron into cobalt and formation of solid solutions of $\text{BaFe}_{0.9-y}\text{Y}_{0.1}\text{Co}_y\text{O}_{3-\delta}$ by solid-phase synthesis, the samples were prepared in the composition range $0.0 \leq x \leq 0.2$ in steps of 0.05.

X-ray data states that the substitution of iron for cobalt leads to the formation of solid solutions of $\text{BaFe}_{0.9-y}\text{Y}_{0.1}\text{Co}_y\text{O}_{3-\delta}$.

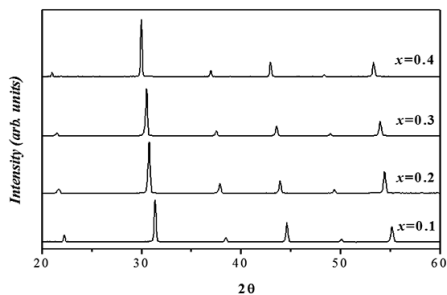


Fig. 1 X-ray data of solid solutions
 $\text{BaCo}_{1-y}\text{Y}_y\text{O}_{3-\delta}$

Homogenous spectrum of complex oxides $\text{BaFe}_{0.9-y}\text{Y}_{0.1}\text{Co}_x\text{O}_{3-\delta}$ extends to the content of cobalt in 0.15.

With the introduction of cobalt in the same sublattice in $\text{BaFe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$, a monotonic decrease of the parameters and scope of the cells of solid solutions

$\text{BaFe}_{0.9-y}\text{Y}_{0.1}\text{Co}_x\text{O}_{3-\delta}$ is observed, which is explained by the size effect.

Change in the oxygen non-stoichiometry (δ) in $\text{BaCo}_{1-x}\text{Y}_x\text{O}_{3-\delta}$ and $\text{BaFe}_{0.9-y}\text{Y}_{0.1}\text{Co}_x\text{O}_{3-\delta}$ from the factual temperature (in the range of 273–1373 K) was studied by thermogravimetric analysis (TGA) in air. The absolute value of the oxygen deficit in $\text{BaCo}_{1-x}\text{Y}_x\text{O}_{3-\delta}$ and $\text{BaFe}_{0.9-y}\text{Y}_{0.1}\text{Co}_x\text{O}_{3-\delta}$ is determined by iodometric titration. For the composition of $\text{Ba-FeO}_{3-\delta}$ value of the oxygen content was determined by direct reduction of the sample in a stream of hydrogen.

With the gradual substitution of cobalt into yttrium in $\text{BaCo}_{1-x}\text{Y}_x\text{O}_{3-\delta}$ within the cubic structure at temperatures <700 K a monotonous decrease in oxygen is observed³.

It has been shown that the introduction of cobalt in iron position in $\text{BaFe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ leads to a decrease in the oxygen content of the samples, (see Fig. 3).

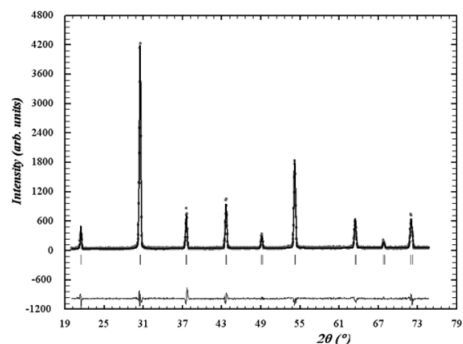


Fig. 2 X-ray pattern of the sample
composition $\text{BaCo}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$, treated by
the method of Rietveld

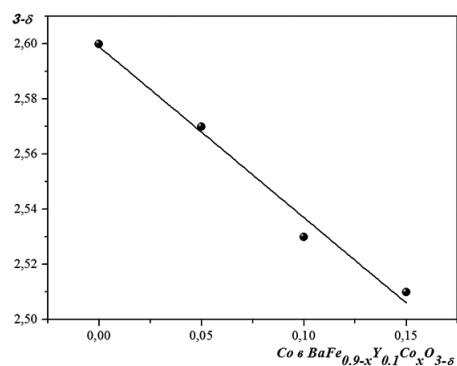


Fig. 3 The dependence of the oxygen content
of the cobalt content in $\text{BaFe}_{0.9-x}\text{Y}_{0.1}\text{Co}_x\text{O}_{3-\delta}$

Because injected in B-sublattice cobalt facilitates vacant disordering of the oxygen lattice, it becomes fully or partially electron acceptor ($\text{EO}_{\text{Co}} = 1.7$; $\text{EO}_{\text{Fe}} = 1.64$)⁴.

To compensate for the excess negative charge of the acceptor defects in the structure of the oxide, an equivalent number of positive ones appears from the oxygen vacancies and / or electronic holes.

Conclusions

Methods of synthesis are worked out and the boundaries of the existence of solid solutions $\text{BaCo}_{1-x}\text{Y}_x\text{O}_{3-\delta}$ ($0.0 \leq x \leq 0.4$), $\text{BaFe}_{1-x}\text{Y}_x\text{O}_{3-\delta}$ ($x = 0.1$) and $\text{BaFe}_{0.9-y}\text{Y}_{0.1}\text{Co}_y\text{O}_{3-\delta}$ ($0 \leq x \leq 0.15$) at 1373 K in air are determined. The parameters of the unit cells studied in solid solutions are calculated and their dependences on the composition of complex oxides are built. It is found that by increasing the degree of substitution of cobalt into yttrium in $\text{BaCo}_{1-y}\text{Y}_y\text{O}_{3-\delta}$, a monotonic increase in lattice parameters is happening, when substituting iron for cobalt in $\text{BaFe}_{0.9-y}\text{Y}_{0.1}\text{Co}_y\text{O}_{3-\delta}$

the reduction of parameters and volume of the cells of solid solutions is happening that is explained by the size effect. For $\text{BaCo}_{1-y}\text{Y}_y\text{O}_{3-\delta}$ and $\text{BaFe}_{0.9-y}\text{Y}_{0.1}\text{Co}_y\text{O}_{3-\delta}$ the dependence on the temperature of the oxygen non-stoichiometry in the air is obtained. It is shown that the oxygen content in complex oxides decreases with increasing temperature. By gradually replacing cobalt into yttrium in $\text{BaCo}_{1-y}\text{Y}_y\text{O}_{3-\delta}$ oxygen content within the cubic structures decreases monotonically. In $\text{BaFe}_{0.9-y}\text{Y}_{0.1}\text{Co}_y\text{O}_{3-\delta}$ with increasing cobalt content oxygen decreases.

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